



CHAPTER 2

EXPERIMENTAL TECHNIQUES

Chapter 2

Experimental Techniques

2.1. Introduction

The present chapter demonstrates material applied for proposed research work and corresponding methodologies of membrane synthesis and their gas permeability techniques. The experimental part involves membrane synthesis process, its gas permeation test and additional characterization techniques. The whole information regarded to the analytic systems and their sources are explained in this chapter. The fabrication of membrane materials was done using variety of modifications such as metal coted polymer membranes, blend polymer membranes, nanofiller dispersed composite and blend composite membranes. Gas transport properties of barrier materials have been characterized by single gas permeation test under fixed test conditions. The base materials and gasses used for this work are mentioned in the section 2.2. The polymer membrane synthesis process is described in detail with the necessary diagram in section 2.3. The fabrication of metal coated PC membrane was done by sputtering process using Pt-Pd metal alloy and Ir metallic substance. MMMs were developed by solution cast method using silica nanofillers. Other sets of blend and blend composite membrane were prepared by solution blending method using PC and PSF with same inorganic nanofillers. Gas permeability techniques applied to test the gas transport through the membrane is explained in the section 2.4. The detailed information of the techniques including its principle, functionality and procedure is described in this section. Subsequently, some additional characterizations are also involved to analyze different properties of developed membranes in section 2.5. The characterizations involve the determination of surface analysis and thermodynamic properties. **Table 2.1** provides the summary of fabricated membranes, the gas permeation techniques, gasses used and additional characterization methods applied to test a particular membrane.

Table 2.1 Summary of Membrane materials and experimental techniques

Polymer Membranes	Gas Permeability Test			Gases	Characterization Techniques
	a	b	*c		
PC (commercially available)	✓			H ₂ , He, CO ₂ , O ₂ , N ₂	DMA, DSC
PC/Pt-Pd	✓			H ₂ , He, CO ₂ , O ₂ , N ₂ , CH ₄	SEM
PC/Ir	✓			H ₂	
PNC (10 wt% SiO ₂)	✓			H ₂	SEM, DMA, DSC
PNC (15 wt% SiO ₂)	✓			H ₂	
PC and PSF		✓	✓	H ₂ , CO ₂ , O ₂	
PC and PSF (with 5 wt% SiO ₂)		✓	✓	H ₂ , CO ₂ , O ₂	**SEM, DMA, DSC
PC/PSF blend		✓	✓	H ₂ , CO ₂ , O ₂	DMA, DSC
PC/PSF Blend (with 5 wt% SiO ₂)		✓	✓	H ₂ , CO ₂ , O ₂	DMA, DSC

➤ “a” denotes constant volume/variable pressure system, “b” denotes constant pressure/ variable volume system and “c” denotes differential pressure system for gas transmission rate.

➤ *Gas transmission rate was obtained for oxygen gas.

➤ **SEM analysis was performed for 5 wt% PC/SiO₂ nanocomposite membrane.

2.2. Materials

2.2.1. Pure and composite membranes

Polymeric material used for membrane was bisphenol-A polycarbonate having average molecular weight of 290.315 g/mol as host polymer matrix and several PC membranes were modified using vapour deposition method and solution cast method. The other polymer was bisphenol-A polysulfone for blend having average molecular weight of 442.54 g/mol. **Figure 2.1 (a)** and **Figure 2.1(b)** show repeating unit of bisphenol-A polycarbonate and bisphenol-A polysulfone respectively [1]. The solvent used was analytical grade dichloromethane (DCM) having chemical formula CH_2Cl_2 .

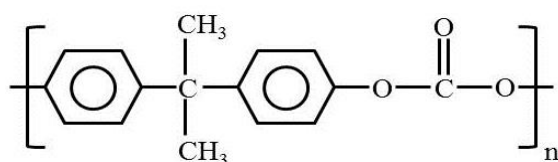


Figure 2.1(a) Repeating unit of bisphenol-A polycarbonate [1]

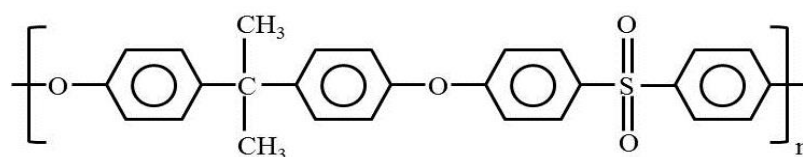


Figure 2.1(b) Repeating unit of bisphenol-A polysulfone [1]

For metal coating, platinum-palladium (Pt-Pd) alloy and iridium (Ir) were used. To prepare MMMs with dispersion of nanofillers silica nanoparticles were used. Silica nanoparticles (stock number 4860MR) were supplied by Nanostructure and Amorphous Materials, Inc, USA and their physical properties are listed in the **Table 2.2**.

Table 2.2 Physical properties of SiO_2 nanoparticles

Properties	SiO_2
BET Surface area	$160 \text{ m}^2 \text{ g}^{-1}$
Density	$2.17\text{-}2.66 \text{ g cm}^{-3}$
Particle size (average diameter)	20 nm
Color	White

2.2.2. Gasses for permeation

Gases used for the permeability test, ranges from kinetic diameter 2.6 Å- 3.8 Å such as He, H₂, CO₂, O₂, N₂ and CH₄ listed in below **Table 2.3**. The gasses are used in high purity up to 99.99 %.

Table 2.3 Kinetic diameter of gases

Gases	He	H ₂	CO ₂	O ₂	N ₂	CH ₄
Kinetic diameter (Å)	2.6	2.89	3.3	3.46	3.64	3.8

2.3 Membrane fabrication

2.3.1. Metal coated polycarbonate membrane

Coating of ultrathin defect free layer on polymer substrate is a challenging task to obtain better transport properties and gas separation efficiency. For the deposition of inorganic coating layer, chemical vapour deposition technique is being used. In this process volatile precursors are transported through vapour phase and decompose on the host substrate producing thin coating layer. The technique is applicable for polymer surface modification by deposition of coating layer and also controls its pore size by maintaining the layer thickness. The thickness of deposition can be controlled by maintaining the material density which is to be ejected on the substrate. For fabrication of layered polymer membranes, gas phase can be converted in to thin films by using this methodology as compared to other methods [2, 3].

The neat polycarbonate membrane was commercially available. It was purchased from General Electrical Co, USA. The thickness of pure PC membrane was about 180 (± 2) μm and coating layer of Pt-Pd alloy was deposited by standard vapour deposition sputtering technique at ICMB facility of University of Texas at Austin, TX, USA. In sputtering process, substrate and target were placed inside vacuum chamber which was evacuated at 10^{-6} torr. In this process, highly energetic bombarding particles were physically ejected by momentum transfer and deposited on the host PC membrane. Relative distance between source and substrate was measured before and after sputter deposition

process at different angles. The average distance and mass measurement of deposited film provides the information to calculate the thickness of coating alloy material. The film thickness measurement was obtained by calculating average distance and measuring amount of deposited material. The calculated, Pt-Pd coating layer was build-up around 8-10 nm and the cross verification of coating thickness was performed by thickness monitor attached with the system. The Ir coated PC membrane was also developed by using the same method [4, 5]. The surface area and thickness of the membrane are given in the **Table 2.4**.

Table 2.4 Surface area and thickness of pure PC, metal coated PC and PC/SiO₂ membranes

Material	Thickness (μm)	Surface area (cm^2)
PC	180 ± 2	1.96
PC/Pt-Pd	180 ± 2	0.6529
PC/Ir	180 ± 2	0.0707
PC/SiO ₂ (10 wt%)	42.8	0.2587
PC/SiO ₂ (15 wt%)	40	0.2826

2.3.2. Silica nanocomposite polycarbonate membrane

MMMs were prepared by inorganic nanofillers into polymer matrix. Polymer nanocomposite membranes were fabricated by solution cast method at different loading percentages of inorganic nanoparticles in the polymer matrix. Solution cast method is convenient technique for synthesis of MMMs [6-8]. As shown in the **Figure 2.2**, polymer material and nanofillers were dissolved individually in the solvent and then the mixture was placed for sonication before casting the membrane in the Petri dish. Due to agglomeration of silica nanoparticles, they do not disperse uniformly in the polymer matrix. Therefore, the mixture was subjected to additional sonication.

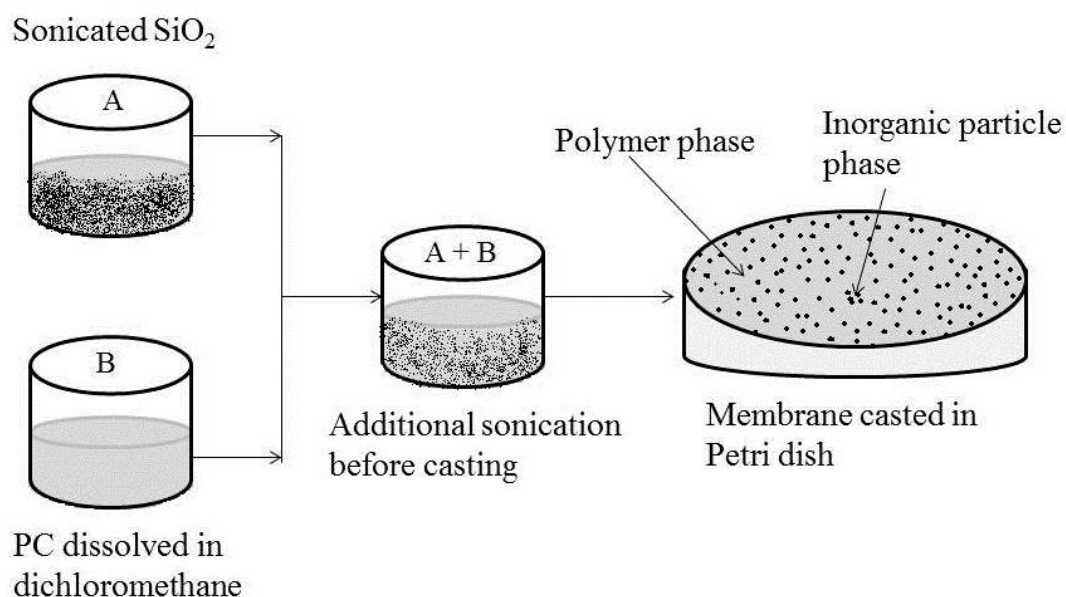


Figure 2.2 Synthesis of nanocomposite by solution cast method

Two different weight percentages i.e. 10 wt% and 15 wt% SiO_2 in PC were used to synthesize nanocomposite membranes of around 40 μm thickness using solution cast method. In this method, a desired quantity of PC was dissolved in the dichloromethane and the mixture was stirred overnight at room temperature using magnetic stirrer. The next day, silica nanoparticles were placed in a sonicator for a period of 5-6 hours. They were allowed to disperse for additional sonication with polymer solvent for 30 minutes before casting the membrane. Then the mixture was poured on a flat-bottomed glass surface. The system was kept overnight for complete evaporation of solvent. These membranes were peeled-off on next day and used for permeability measurements. The uniformity in thickness of membranes was confirmed by digital thickness meter. The surface area and thickness of these MMMs are mentioned in the **Table 2.4**.

2.3.3. Nanosilica doped PC/PSF blend composite membrane

The solution cast technique explained in the previous section was applied to develop blend, composite and blend composite membranes at our laboratory. Bisphenol-A polycarbonate and bisphenol-A polysulfone were used in fine grain size for synthesis process. At the beginning, all the glassware

were cleaned with double distilled water and acetone. Desire quantity of PC and PSF were measured by digital weigh machine relative to the area of petri-dish and consideration of particular thickness of the membrane. Different blending ratios of PC/PSF such as 80:20 and 40:60 were developed with respect to PC wt% of blend membranes. Moreover, pure PC and pure PSF membrane were also prepared by the same method for comparison of final outcome due to blending effect. The same set of blend and pure samples was synthesized by SiO₂ nanopartilces by performing additional sonication before casting. For pure PC membrane, desire quantity of PC was stirred with dichloromethane on a magnetic stirrer for 3 hours and then the solution was poured in a petri-dish by keeping it for overnight. Next day, the membrane was peeled-off from the petri-dish. For blending, different ratios of PC and PSF were stirred separately with dichloromethane for an hour using magnetic stirrer. The solutions were mixed in a beaker and then placed for 2 hours on magnetic stirrer. After completing the stirring process the resulting solution was poured in a petri-dish keeping it overnight and was peeled-off. To prepare SiO₂ doped blend membrane, the blending process same as blend membrane had been performed up to the final blend solution was obtained. Silica nanoparticles were added to dichloromethane and the mixture was stirred for 15 minutes and was mixed with the final blend solution which was sonicated for 5 minutes. After sonication, the resultant mixture was stirred overnight. Next day, the mixture was kept for sonication for 40 minutes then stirred for 5 minutes and finally poured in a petri-dish. Further it was kept overnight and next day it was peeled-off. The appearance of the developed membrane is shown in **Chapter 5**.

The thicknesses of developed membranes were determined by thickness-meter at Labthink, Jinan, China. Although accuracy was maintained at the time of membrane casting process but eventhough the whole area of developed membrane might not be considered as uniform at each and every point. Therefore, small portion of the tested membrane was mounted in Al foil tap in such a way only small exposed area can be available for gas permeation. The

aluminum foil transports gas flux in very negligible amount which will be discuss later in the section 2.4. Exposed area of the test membrane was determined by ImageJ software. The membrane was zoomed at fixed distance and its image was recorded in unit of pixels. Using imageJ software, the area of recorded membrane images was estimated. The thickness and exposed area of the developed membrane are listed in the **Table 2.5**.

Table 2.5 Membrane thickness and exposed area

Material	Thickness (μm)	Area (cm^2)
PC	50	1.88
PSF	25	1.76
PC/SiO ₂	49	1.76
PSF/SiO ₂	40	1.69
PC ₈₀ -PSF ₂₀	46	1.62
PC ₈₀ -PSF ₂₀ /SiO ₂	30	1.74
PC ₄₀ -PSF ₆₀	28	1.78
PC ₄₀ -PSF ₆₀ /SiO ₂	27	1.78

2.4 Gas permeation techniques

The experimental set up of gas permeation testing mainly consist apparatus made up of standard stainless steel (SS 316) components. The system arrangement consist mainly three units: (a) supply of gas flux by a gas feed line arrangement towards high pressure chamber side, (b) a tightly sealed sample holder and (c) analysis part where permeate gas is collected and its flow rate is determined. The gas permeation systems utilized are explained as per different mechanisms.

2.4.1 Constant volume/variable pressure method

In this technique, the downstream pressure from the permeated side is recorded as a function of time. Pressure transducer was used to determine the rate of transported amount of gas. The permeability of H₂, He, CO₂, O₂, N₂ and

CH₄ was measured using a constant volume/variable pressure method at CEER, The University of Texas at Austin, USA [9]. Commercially available PC, metal coated PC and silica nanocomposite PC membranes with 10 wt% as well 15 wt% filler content were tested by this technique.

The output obtained by the constant volume/variable pressure system was recorded as function of change of pressure with respect to time from downstream side of the gas permeability cell according to Fick's law of diffusion. Software was developed at UT, Austin, Texas, USA for recording the data. As illustrated in the **Figure 2.3** the system includes vacuum gauge to determine the small variation due to transport of gas molecules. The system consists gas permeation cell which is attached with vacuum pump. Towards the upstream side of the cell, a gas supply unit consists of a regulator attached with the cell and the permeated side is connected with a pressure transducer to measure pressure variations.

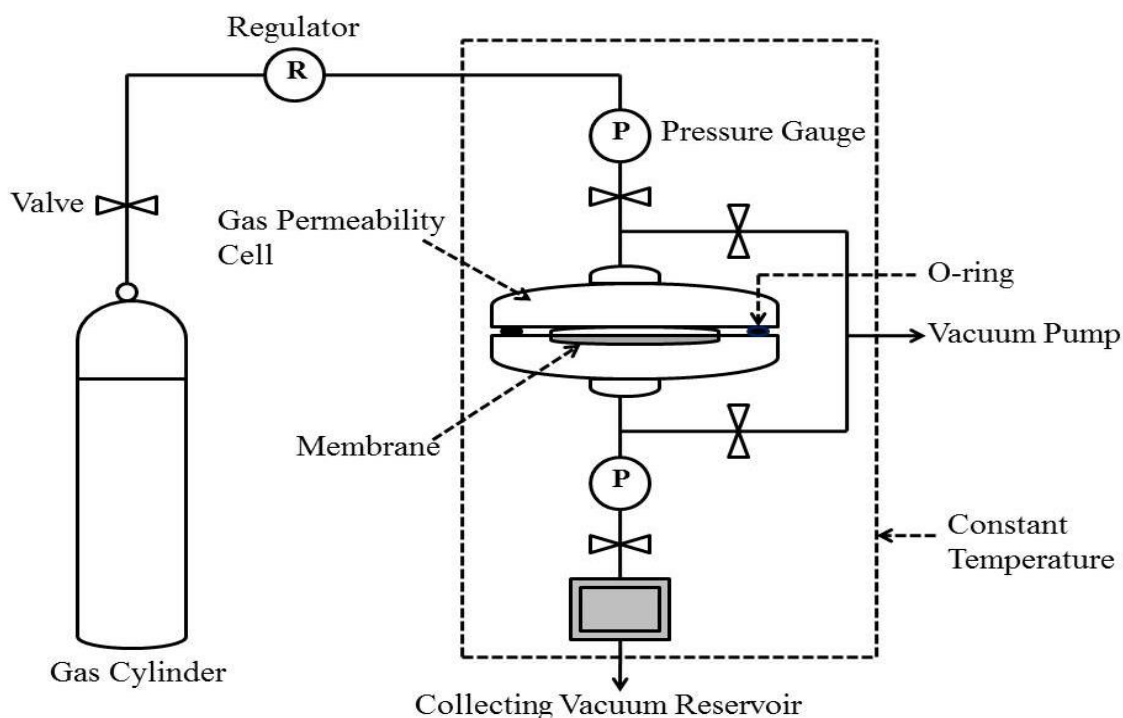


Figure 2.3 Constant volume/variable pressure system

The amount of gas permeate through the test film was measured by monitoring the downstream pressure in a closed volume using a pressure transducer. For accurate measurements, the system was subjected to vacuum

prior to remove any volatile impurity inside the system. Thus the feed volume and permeate volume were evacuated to degas the film. After closing the valves connecting the permeation cell to vacuum pump, slow pressure raised towards downstream volume called the leak rate of the system and this leak rate should be around 10 times less than the steady state permeation of gas flow. Therefore, vacuum should be maintained properly to fulfil the operational requirement. Then the feed gas was supplied to the cell from upstream side of the membrane and at the downstream side the variation in pressure was recorded as function of time. The experiment was performed at constant operating pressures 30 psi and at constant temperature 35 °C. To determine plasticization effect due to CO₂ for PC/Pt-Pd membrane, the test was performed within the operating pressure range from 30 psi to 230 psi. Inside the gas permeation cell, the coated side of the membrane was faced towards feed side. Following equation 2.1 was used to calculate the permeability coefficient:

$$P = \frac{l}{P_2 - P_1} \cdot \frac{V}{ART} \cdot \left[\left(\frac{dP_1}{dt} \right)_{ss} - \left(\frac{dP_1}{dt} \right)_{leak} \right] \quad 2.1$$

Where, P is the gas permeability coefficient, V is total volume of downstream side which is 39.43 cm³, l is thickness of the membrane in cm, P₂ is upstream absolute pressure in psig, (dP₁/dt)_{ss} is the steady state slope of downstream pressure versus time calculated in cm-Hg/s, (dP₁/dt)_{leak} is the leak rate calculated in cm-Hg/s. During the experiment, the leak rate was maintained up to 10⁻⁷ cm-Hg/s. Permeability was calculated in barrer, where 1 barrer = 10⁻¹⁰ [cm³ (STP) cm/ (cm² s cm-Hg)].

2.4.2 Constant pressure/variable volume method

A constant pressure variable volume system measures the amount of gas flow permeated through the membrane in the form of volumetric flow with respect to time [10]. This method is used for relatively high permeation membrane system. The system has been established at our laboratory using

stainless steel gas permeation cell and a mercury flowmeter. The amount of gas flux permeated through the downstream volume of gas permeability cell is either supplied to the soap bubble flowmeter or to the mercury flowmeter as per the membrane material utilized for the analysis. Usually, rubbery polymer membranes transport higher gas flux as compared to the glassy polymer membranes. Therefore, for both types of membrane materials this method is applicable. Permeability cell made of SS-316 material was manufactured by Gayatri Engineering (GIDC Ind Estate, Makarpura, Vadodara) and the flowmeter was manufactured by Baroda Scientific Glass Works (Sardar Bhavan Lane, Vadodara). The flow rate of H_2 and CO_2 was measured by mercury flowmeter containing small mercury slug.

The output obtained by the constant pressure/variable volume system was recorded as function of change of volume with respect to time from downstream side of the gas permeability cell. Gas permeability cell is key part for this developed system made of two cylinders of stainless steel 316 material as shown in the **Figure 2.4**. Towards the feed side, a pressure gauge was attached providing maximum pressure up to 150 psi and V1 represents the inlet valve to feed the gas inside the cell. Valve V2 was used for purging gas or the air impurities from the inert volume of the cell. The cell has been developed with taper threading to connect the valves, pressure gauge and outlet nozzle. Especially for the gas testing applications, taper threading at joining parts gives better clearance to prevent gas leakage from the system. Membrane was placed inside the lower cylinder with porous support. Two distinct diameter O-rings were placed inside the lower cylinder concentrically to conform accurate test measurement providing necessary seal. Larger O-ring was used to seal the cell, creating leak free seal at the connecting edges of both the cylinders. In order to prevent feed gas escaping directly from feed side in to downstream phase, smaller one was used to create seal on the surface of test membrane. The function of O-ring at the connecting edges is to create seal between gas flux from upstream and downstream side. The central O-ring is of same diameter of central outlet to prevent gas flow from the membrane edge. Similar way at each

and every joining of the permeation cell O-rings were used to prevent gas leakage from the cell. Silicone grease was used to apply on the surface of O-rings to ensure adhesion against higher pressure. Both the cylinders of gas permeability cell were sealed with six fully threaded hex screws.

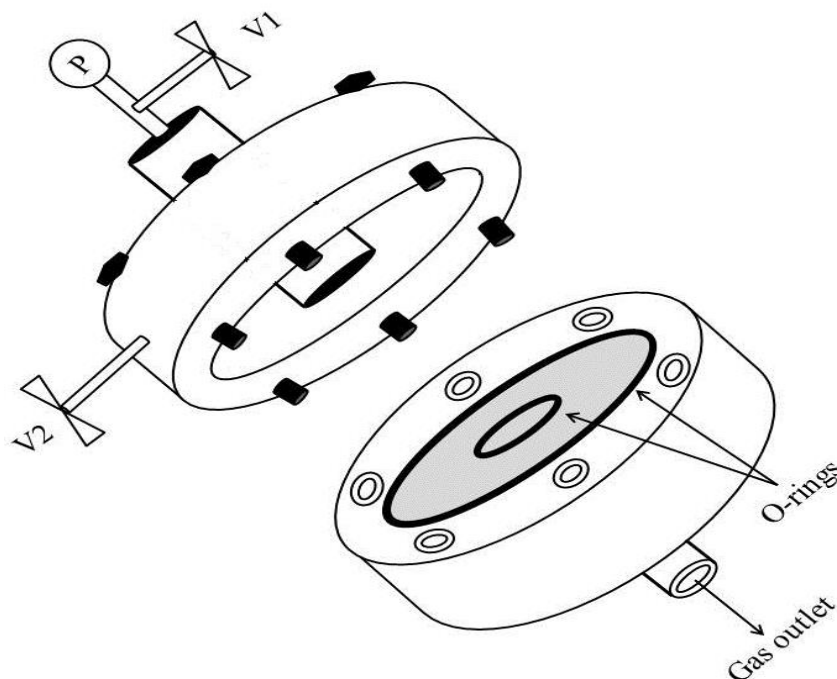


Figure 2.4 Schematic diagram of gas permeability cell

A schematic diagram of the system established in our laboratory is shown in **Figure 2.5** and **Figure 2.6**. As shown in the **Figure 2.5**, gas permeability cell is connected with the gas cylinder through regulator from upstream side and the downstream volume was released into mercury flowmeter filled with small mercury slug. Dual pressure gauge was attached with the gas cylinder to control higher pressure from the gas cylinder in to comparative low pressure gauge connected with the cell. If the gas flux is applied from the gas cylinder into permeation cell directly then there is possibility of breaking the system and may cause harm due to sudden flow of very higher pressure. Thus the function of dual pressure gauge is to prevent the established system from an accident. To record the raise in mercury height, centimeter scale is attached with the flowmeter. The flowmeter was made of transparent capillary material with 2 mm inner diameter. It was rinsed by silicone oil to provide smooth flow of mercury slug within the capillary. The

raise in mercury height gives rate of transport of gas molecules through the membrane.

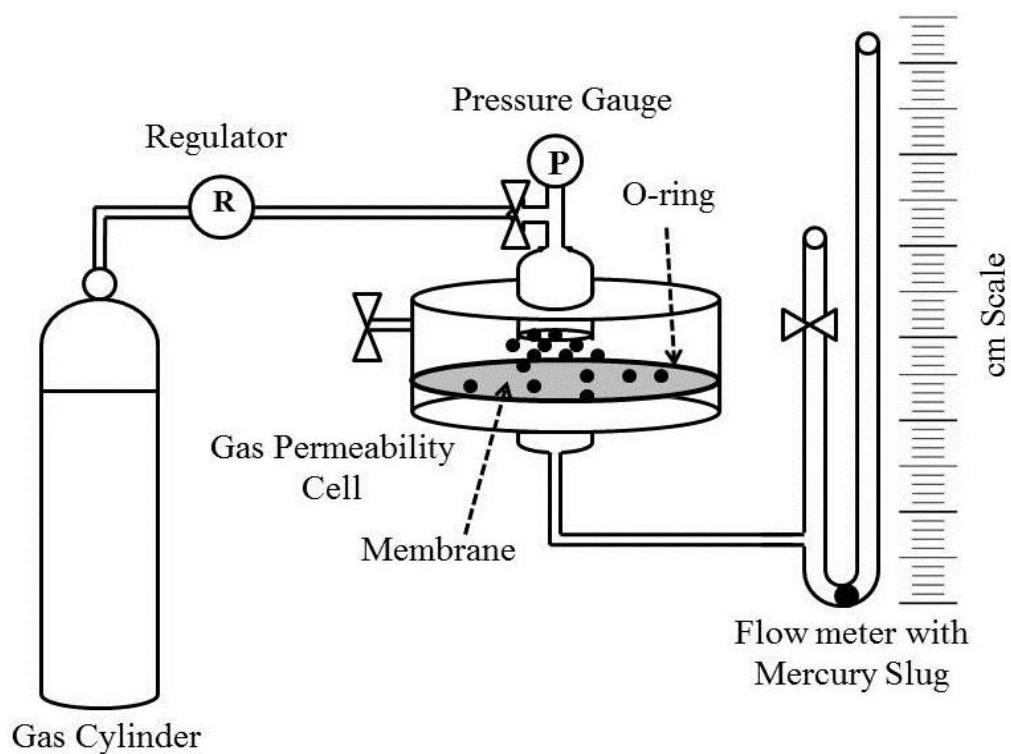


Figure 2.5 Schematic diagram of constant pressure/variable volume system



Figure 2.6 Image of constant pressure/variable volume apparatus

As shown in the **Figure 2.6** the feed gas supplied by gas cylinder enters through the valve connected between the cylinder and feed side of the gas permeability cell. Before beginning the measurements, upstream and the downstream sides were purged with the feed gas twice or thrice to remove any impurities and to achieve better transport rate of the applied gas stream. The target gas was supplied at constant pressure towards upstream face of the membrane and steady-state gas flux was measured from the downstream side of the membrane in the mercury flowmeter. The rate of change of the gas molecules transported through the membrane can be recorded by the movement of the mercury slug inside the fine capillary of the flowmeter which was attached with the centimeter scale. As shown in the **Figure 2.6**, the cell was attached with the hydrogen cylinder and constant 30 psi operating pressure applied at room temperature to the polymer membrane to be tested. Initially, mercury slug was set at particular height at the upper side of the curved portion of the flowmeter using a bubbler through the opening valve. The system was degassed twice using the feed gas before starting the experiment for accurate measurement. After the purging process, experiment was performed at constant 30 psi operating pressure. The gas molecules permeated through the membrane towards downstream side flows within the mercury flowmeter. As the gas expanded in to the flowmeter capillary containing mercury slug, displaced upward as the permeated gas pushed it. Its movement offers direct measurement of rate of gas flux permeating through the membrane. The rise in mercury height was recorded as a function of time. By multiplying the rate of change of mercury slug height with the capillary area will give rate of change of volume of permeated gas by the polymer membrane. The experiment was repeated twice to achieve accurate measurement. The steady-state permeability of the system is given by the following equation **2.2**:

$$P = \frac{l}{P_2 - P_1} \cdot \frac{P_{\text{atm}}}{ART} \cdot \frac{dV}{dt} \quad 2.2$$

where, l is the thickness of the membrane in cm, P_{atm} is the atmospheric pressure i.e. 1 atm, dV/dt is the rate of change of gas flux permeated through

the membrane, $(P_2 - P_1)$ is the pressure difference of upstream side and downstream side of the membrane. As downstream pressure is very negligible as compared to upstream pressure, in calculation only P_2 is considered. A is the exposed area in cm^2 , R is the universal gas constant in $\text{cmHg}\cdot\text{cm}^3/\text{cm}^3(\text{STP})^\circ\text{K}$ and T is the room temperature. The gas permeability measured by this system was calculated in unit barrer.

The plot of height gain of mercury slug versus time gives the slope dh/dt which is multiplied with capillary area giving rate of variable gas volume permeated through the membrane. Hence, the equation 2.2 is given in below form where ‘a’ is the capillary area of the mercury flowmeter.

$$P = \frac{l}{P_2 - P_1} \cdot \frac{P_{\text{atm}}}{ART} \cdot a \cdot \frac{dh}{dt} \quad 2.3$$

Polymer materials applied for the test were glassy polymers which give low transport rate for gas permeation. Therefore, small amount of leakage cannot be avoided while performing the test. To check the system leakage, an experiment was performed by placing aluminum foil instead of membrane at 30 psi upstream pressure for 48 hours using air as penetrant. There was no pressure drop and also the height of mercury slug was also remained same for two days. It suggests that within 48 hours aluminum foil do not permeate the air molecules. Before considering aluminum foil for the test, it was analyzed for oxygen transmission rate (OTR). Oxygen transmission rate of the membranes as well aluminum foil was determined by gas transmission rate apparatus (i-Gastra 7100 Gas Permeability Tester) at Lab Think (Jinan, China) which will be discussed in section 2.4.3. The oxygen transmission rate of aluminum foil is very negligible i.e. 1000 times less than the membrane used up to 24 hour at 30 psi feed pressure and 35 °C. Thus the aluminum foil would be an ideal material used to scrutinize gas leak from our presented system.

2.4.3 Differential pressure method for gas transmission rate

In the differential pressure method, the test chamber is divided into two independent parts by sample mounting. Test gas is filled at the one side of the chamber with absolute pressure and the other side is evacuated creating particular pressure difference. Pressure difference is created towards the lower pressure chamber as the test gas transmits through the test membrane or film. Gas transmission rate can be calculated by pressure variation observed by very high precision vacuum gauge [11]. The instrument utilized for this test is i-Gastra 7100 Gas permeability tester working on the differential testing method for the gas transmission rate. The instrument diagram is shown in the **Figure 2.7**. It is embedded with computer control system and intelligent operating software. It conforms international standards such as ASTM, ISO, JIS etc. This instrument can determine gas transmission rate of dense as well porous films, sheets, glass fiber cloth, soft tube material for cosmetics etc.



Figure 2.7 i-Gastra 7100 gas permeability tester

The system works on the principle of differential pressure method for gas transmission rate. Pressure gradient is created across the specimen and gas transmission rate from lower chamber is recorded as a function of time. The whole system is integrated with three test cells gives separate permeability for each at same time duration which improves test efficiency of the instrument. Moreover, an average of three different outputs can also be obtained at same time for same materials with different species. Computer system embedded within the equipment provides safer and reliable data management and the test

operation, which is fitted with USB port and internet port for convenient data transmission. The instrument is also equipped with vacuum system that can amend the output at particular operating pressure. Diffusion coefficient, solubility coefficient and permeability coefficient can be directly determined by this instrument. It consist humidity control range as well temperature control which supports different test conditions. At extreme conditions, test results can be obtained by data curve fitting function at any temperature and the test range can be extended to fulfill requirements of high and low permeability materials. The system can be customizing to cover the test of explosive gases. The design and functionality of the system chose it for accurate and fast calibration.

The specimen was placed inside the permeability cell which separates it in the upper chamber and the lower chamber is clamped tightly. Feed gas was applied from the upper chamber and transmitted from the lower chamber. First of all, the low pressure chamber was evacuated and then the whole system was vacuumed. As vacuum was achieved up to specified degree, lower chamber shut off and test gas was feed to the upper chamber until certain pressure achieved. It is necessary to ensure constant differential pressure across the test specimen. The pressure difference between the upstream side and the downstream side becomes the driven force for gas permeation. As the gas molecules permeated through the film, the pressure on the other side of the film increased which was measured over time. By finding the slope of gain in pressure with respect to time once it becomes linear, the gas transmission rate across the specimen can be calculated. Gas transmission rate was obtained in the unit $\text{cm}^3/\text{m}^2 \cdot 24\text{h} \cdot 0.1\text{MPa}$. Thus under the differential pressure gradient, feed gas permeates from higher pressure side to lower pressure side. By obtaining the rate of gas flow through the specimen, various barrier parameters can be determined. Gas transmission rate or permeance can be calculated by the equation mentioned below;

$$\text{GTR} = \frac{V}{P_2 A R T} \cdot \frac{dP_1}{dt} \quad 2.4$$

Where P_2 is the applied pressure, A is the effective gas exposed area, R is the universal gas constant, T is the test temperature and dP_1/dt represents pressure difference towards low pressure side per unit time as the transmission rate becomes stable. Permeability of the thin film or the membrane can be calculated by the formula given in the **Chapter 1**.

2.5 Additional characterization techniques

2.5.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope is a versatile instrument utilized to examine the microstructural morphology of chemical compositions. The schematic diagram of SEM is given by the **Figure 2.8**. An electron gun is located at the top of the column which produces the electrons along with accelerating them towards the sample holder. Hairpin tungsten gun is utilized to produce large electron beam diameter for the development of high image resolution. The electromagnetic lenses and apertures are used to focus the electron beam on the specimen. The real-time observations and image recording of the specimen surface can be obtained by specimen stage, scanning coils, signal detector and processing system [12].

FE-SEM analysis was performed for PC/Pt-Pd and PC/SiO₂ (10 wt% filler amount) membranes at University of Texas at Austin, USA using Carl Zeiss instrument as shown in the **Figure 2.9**. Initially, the membrane was coated with a very thin layer of platinum/palladium alloy of about 8 nm in thickness keeping in sputtering prior and then the sample was placed in the SEM chamber. The width of sample beam was kept 4.7 mm and an InLense detector was used to monitor the output. The SEM image and its explanation will be described in **Chapter 3** and in **Chapter 4**.

The surface morphology of PC/SiO₂ membrane was determined by JSM 5810 LV (JEOL Ltd.) scanning electron microscopy (SEM) at the Department of Metallurgical and Materials Engineering, MSU, Vadodara which will be discussed in **Chapter 5**. The system image is given by **Figure 2.10**.

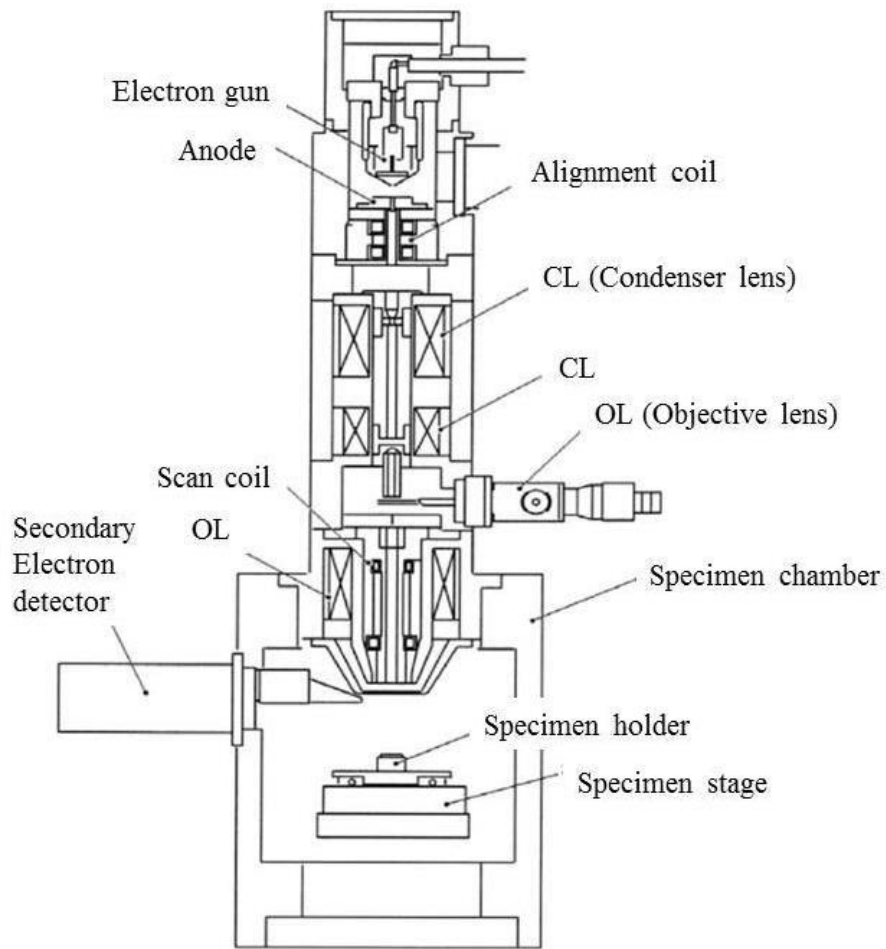


Figure 2.8 Schematic diagram of SEM [12]



Figure 2.9 Carl Zeiss SEM instrument



Figure 2.10 JSM 5810 LV (JEOL) SEM instrument

2.5.2 Differential Scanning Calorimetry (DSC)

The schematic diagram of differential scanning calorimetry is shown in the **Figure 2.11**. The reference and the sample holder are placed inside the heat sink which is surrounded by heater. Any temperature difference in the reference and sample can be obtained by the heat flux recording. DSC measures the temperature and heat flow associated with the transitions in the material as a function of time and temperature. These measurements provide information about the physical and chemical changes which involve endothermic or exothermic reaction occur during the analysis [13].

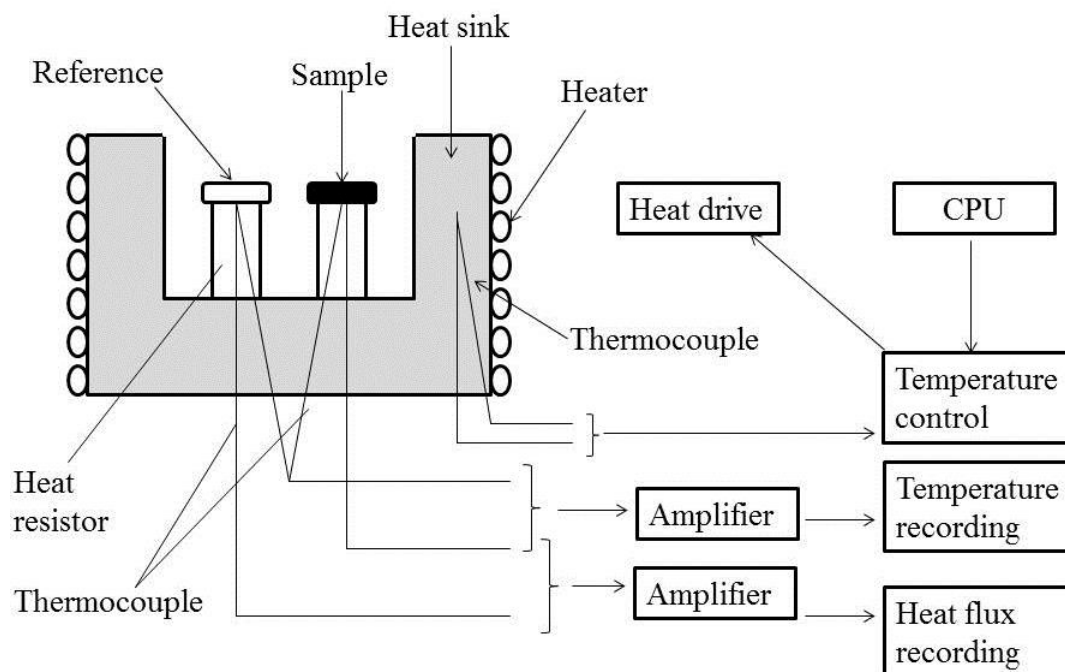


Figure 2.11 Schematic diagram of DSC [13]

The analysis was performed by standard Q-series DSC model using TA Instruments, USA in nitrogen atmosphere as shown in **Figure 2.12**. Pure PC membrane and PNC membrane with 10 wt% SiO₂ nanofillers were analysed using this equipment. The Q-series DSC instruments give superior performance in sensitivity, resolution, baseline flatness and precision. The equipment provides temperature performance from -180 to 725°C with ± 0.01 precision. The detailed analysis about T_g determined by the presented instrument will be discussed in **Chapter 4**.

DSC analysis was applied on polymer blend and blend composite membrane (5 wt% SiO₂) in temperature scan mode by PerkinElmer DSC 8500 as shown in **Figure 2.13**. DSC8500 provides extremely fast control scanning rates up to 750 °C/min. It also provides temperature performance from -180 to 750 °C with ± 0.008 °C precision. In addition, ballistic cooling rate up to 2100 °C/min is also included. To characterize given samples, heat flow was applied from -60 to 350 °C at 20 °C/min in the nitrogen atmosphere. The glass transition temperatures and heat capacity measured by DSC 8500 will be discussed in **Chapter 5**.



Figure 2.12 Q series DSC TA instruments



Figure 2.13 Parkin Elmer DSC 8500

2.5.3 Dynamic Mechanical Analysis (DMA)

In DMA, an oscillatory force is supplied which cause a sinusoidal stress to the sample generating a sinusoidal strain. The amplitude of deformation and the lag at the peaks of stress and strain sine waves are measured. These

parameters are used to calculate modulus, viscosity and damping in the sample to be tested. A schematic diagram of dynamic mechanical analysis is shown in the **Figure 2.14**. A force motor generates sinusoidal waves and it is transmitted to the sample via drive shafts [14].

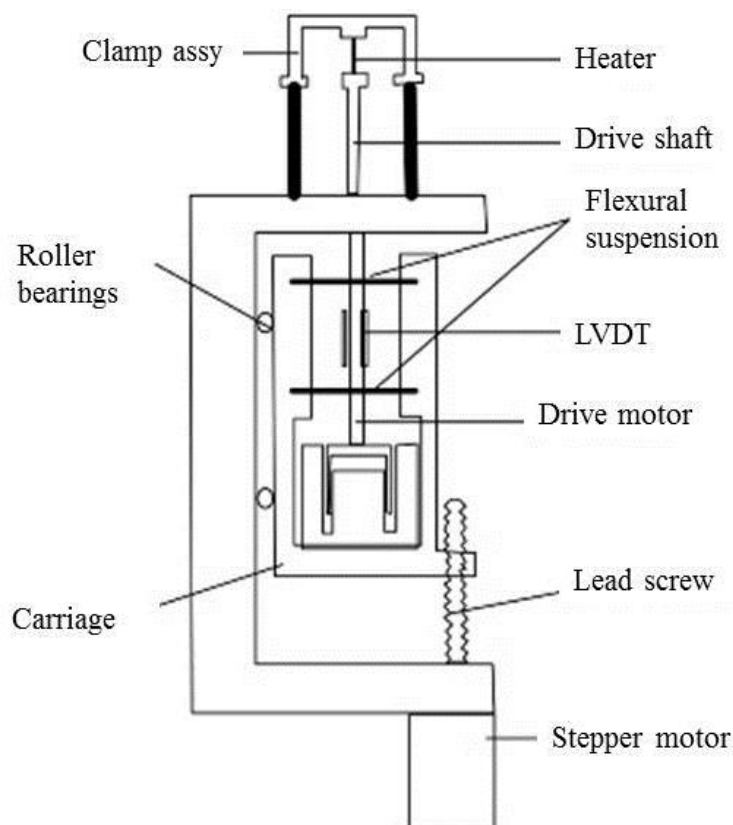


Figure 2.14 Schematic diagram of DMA [14]

DMA analysis of pure PC and 10 wt% silica nanocomposite membranes was performed using TA Instruments, USA by Q800 model which is given in the **Figure 2.15**. It can identify modulus ranges from 10^3 to 3×10^{12} Pa with 0.01 precision. Frequency of 0.01 to 200 Hz can be applied by Q800. The measurement was performed at 25 °C and ramp force 1-18 N was applied in the nitrogen atmosphere. The detailed description of stress verses strain analysis obtained by this equipment will be discussed in **Chapter 4**.

Polymer blend composite membranes (5 wt% SiO₂) were characterized using PerkinElmer DMA 8000 as shown in **Figure 2.16**. DMA 8000 measures change in the rheological behaviours of given sample as function of temperature, time frequency or combination of these parameters. Moreover,

thermomechanical, stress-strain, creep recovery and stress relaxation measurements are also analysed by this instrument. Frequency range from 0 to 600 Hz can be applied with 0.001 Hz resolution by this instrument. Modulus identification from 10^3 to 10^{16} Pa with 0.0001 Pa resolutions can be obtained using this equipment. The samples were tested under the heating rate of temperature scan at 3 °C/min ranges from 30 to 250 °C with tension rectangle measuring system. The measuring sample dimensions are given in below **Table 2.6**. Temperature scan mode was used to measure modulus and damping of the given samples which will be discussed in **Chapter 5**.

Table 2.6 Sample dimensions used in DMA testing

Materials	Length (mm)	Width (mm)	Thickness x 10⁻³ (mm)
PC ₈₀ -PSF ₂₀	10.00	3.70	60
PC ₈₀ -PSF ₂₀ /SiO ₂	10.00	3.05	30
PC/SiO ₂	10.04	6.00	50
PSF/SiO ₂	9.86	5.14	60



Figure 2.15 DMA Q 800 TA Instruments



Figure 2.16 ParkinElmer DMA 8000

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